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COMPLETE SPECIFICATION.

Compositions and Methods for Producing Electrically Conductive Coatings.

We, ACIESON INDUSTRIES, INC., a Corporation organised and existing under the laws of the State of Michigan, United States of America, of Michigan National Bank Chambers, Port Huron, Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to compositions for and the method of producing electrically conductive coatings on supporting surfaces. More particularly, this invention concerns the method of and compositions for the production of coatings on the walls of electron discharge tubes such as cathode ray tubes and more specifically television picture tubes for colour or black and white reception.

The use of conductive coatings in electron discharge tubes is well known, but the previously known and commercially used coatings have shortcomings including softness, poor adhesion, deficient electrical conductivity, excessive shrinkage on drying, difficulty in outgassing and continuing loss of gas during operation or the like. These deficiencies are corrected and other desirable features are obtained by formation of coatings from the coating compositions of the invention.

In the heretofore known compositions for producing conductive coatings that were used on the interior surface of cathode ray tubes the presence of organic constituents was considered to be undesirable. In accordance with this invention, however, it has been found that certain organic com-

pounds, as will be detailed later in this specification, provide improved adherence, hardness and performance characteristics in the resulting coatings on the interior of cathode ray tubes.

Accordingly, the present invention provides a composition for use in forming electrically conductive coatings which comprises, in weight percent, 10% to 25% of a conductive pigment, 15% to 80% of a solution of an alkali metal silicate containing from 42% to 71% water, 0.3% to 5% of a water-soluble or water-dispersible organic resin material, 0.5% to 10% of an alkali metal or ammonium carboxylic acid salt and the balance water.

The conductive pigment used may be selected from such well known conductive powders as conductive carbon black, graphite, which is preferred, metal particles, etc., or mixtures thereof. It has been found that both natural and artificial graphites may be used effectively, and that the particle size or shape of the graphite is not critical, except that the graphite is preferably finely divided, for example, finer than 200 mesh (Tyler Standard Screen Size).

The inorganic binder constituent is the material commonly known as water glass, namely, aqueous solutions of an alkali metal silicate such as the sodium or potassium silicates or mixtures thereof. Any of the commercially available water glass materials may be satisfactorily employed and these materials vary in water content from approximately 42% to 71%, by weight, and have ratios of alkali metal to silicate expressed as percent alkali metal oxide to SiO₂.

[Price 4s. 6d.]

in the range of 1:2 to 1:7, and preferably in the range of 1:2 to 1:3.5.

The organic resin component serves to improve the initial adhesion properties and flow characteristics of the compositions and to maintain the conductive pigment in dispersed condition prior to application to the substrate and during, at least, the initial curing stages of the inorganic binder component. Organic resinous materials for this purpose should be water-soluble or water-dispersible and decomposable at the temperatures normally employed in cathode ray tube manufacture namely 250 to 475°C, leaving a residue which does not generate deleterious gases during subsequent processing and use. Resins possessing these requirements include the water soluble or water dispersible cellulosic resinous materials such as methyl cellulose, sodium carboxymethyl cellulose, hydroxyethyl cellulose, water soluble gums and plant extracts such as agar-agar, Irish moss extract i.e. the extract taken from dried bleach plant of chondrus crispus or gigartina mamilliosa, polyvinylpyrrolidone and polyvinyl alcohols and mixtures thereof. The preferred material for this purpose is polyvinylpyrrolidone since this resin has been found to possess all of the required characteristics to an unusual degree. Polyvinylpyrrolidone is compatible with the silicate binder and decomposable at normal bake-out temperatures for cathode ray tube manufacture. It aids in forming the initial coating on a glass substrate by its film-forming ability and its ability to wet glass. It also appears to maintain the uniformity of the distribution of the conductive pigment in the binder-carrier system as the aqueous carrier is removed during the normal drying of the coating. The lower molecular weight polyvinylpyrrolidone materials are particularly suitable, for example, materials having a molecular weight in the range of about 8,000 to about 50,000.

Cathode ray tube coatings formed from the heretofore known compositions containing graphite and alkali metal silicates have a smooth, hard, glassy surface which overlies a soft, easily abraded lower layer. It has been found to be extremely difficult, if not impossible, to heat cure the alkali

metal silicate to a form that is hard and abrasion resistant throughout its entire depth because the upper glassy surface tends to trap some of the water of hydration during such cure. In accordance with this invention, it has been found that in the presence of the above named ingredients, this problem of the formation of an upper glassy water-impervious layer is eliminated by incorporating into the aqueous compositions a small quantity of an ionizable or disassociatable alkali metal or ammonium carboxylic acid salt. These salts modify the alkali metal silicate binder during dehydration to form a porous coating which remains sufficiently porous throughout the curing operation to permit water or gaseous decomposition products of any of the components in the film to escape. This modification of the film enables the complete removal of all of the water of hydration in the inorganic binder and a substantially complete cure of the binder to a hard abrasion-resistant form. Suitable salts, or film modifiers, for this purpose preferably include the sodium or potassium salts of the monocarboxylic, dicarboxylic, the hydroxy dicarboxylic and hydroxytricarboxylic aliphatic and aromatic acids. The simple salts of the aliphatic acids such as sodium acetate or potassium oxalate or the aromatic acids such as potassium phenylacetate or sodium benzoate may be used but better results have been obtained from the use of more complex salts such as potassium acid tartrate or potassium sodium tartrate. The exact mechanism by which such salts function to improve the adhesion, hardness and abrasion resistance of the resultant coatings is not fully understood but evidence has been obtained which demonstrates that the ions in the aqueous composition which result from their presence, or the same ions from an equivalent source, are necessary in order to avoid the water impervious glassy surface and the easily abraded lower layer, and to provide improved adhesion, hardness and abrasion resistance.

The compositions of this invention contain the above discussed components in the relative proportions set forth below in Table I.

TABLE I

CONDUCTIVE PIGMENT		WEIGHT PERCENT	
5	Graphite, carbon black, finely divided metal, or mixtures	10	—25
	Binder (alkali metal silicate—42%—71% water)	15	—80
	Organic resinous materials (water soluble or dispersible resin)	0.3	—5.0
	Alkali metal or ammonium salt of carboxylic acid	0.5	—10
	Water		Balance

A preferred formulation is set forth in Table II.

TABLE II

CONDUCTIVE PIGMENT		WEIGHT PERCENT	
15	Graphite, carbon black, finely divided metal, or mixtures	12	—20
	Binder (alkali metal silicate—42%—71% water)	35	—75
	Organic resinous materials (water soluble or dispersible resin)	0.75	—2.0
	Alkali metal or ammonium salt of carboxylic acid	1.0	—5
	Water (Distilled or Deionized)		Balance

The compositions of this invention are prepared by simply blending the selected quantity of each of the components and mixing until a uniform dispersion is obtained. No particular order of addition of the components is necessary and any of a variety of standard mixing equipment may be used to form the dispersions.

The method of using this invention broadly comprises the steps of applying a composition of this invention to the substrate to be coated, for example by spraying, brushing, flowing, or roller-coating, to deposit on the substrate the desired quantity of that composition. For cathode ray tube coatings a sufficient quantity of the composition is applied to produce a cured coating thickness in the range of 0.1 to 2 mils. Thereafter, the coating may be preliminarily

dried with, for example, circulating hot air, and is then heat cured at a temperature within the range of 250°C to 475°C until the coating is hard and adherent to the surface generally, for about one-half to about two and a half hours. Alternatively, the preliminary hot air drying step may be omitted and the coated surface slowly raised from room to its final curing temperature. After curing, the coating is optionally water rinsed or may be used in its heat cured condition.

The following Examples illustrate this invention. Example 1 is included by way of comparison.

EXAMPLE I

A coating composition was prepared containing the following materials, in weight percent:

		WEIGHT PERCENT	
60	Graphite (maximum particle size—10 microns)	14.2	
	Polyvinylpyrrolidone (average molecular weight—10,000)	1.5	
65	Aqueous potassium silicate (30° Baume at 68°F, viscosity—7 centipoises at 68°)	9.05	
	19.9% SiO ₂	74.1	
	Deionized water	10.2	

This composition does not contain an alkali metal or ammonium carboxylic acid salt.

The above ingredients were thoroughly mixed for 16 hours in a standard pebble mill. The dispersion removed from the mill was applied to a 3"×6" glass panel, at room temperature, by spraying. The coated panel was cured in an air atmosphere furnace

slowly raised to a temperature of 400°C, with the panel being maintained at 400°C for approximately one hour.

When the panel was removed from the furnace and inspected under a microscope at magnifications up to 60 diameters the coating was observed to be smooth, glassy and free of pores. The coating was measured for electrical resistance and found to have

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a resistance of 126 ohms per square. The adhesion and hardness of the film was tested by scraping a blunt metal blade across the coating. The glassy skin of the film was easily pierced and portions of the coating removed in the form of flakes.

EXAMPLE II

A coating composition was prepared, using similar mixing equipment and procedures as those employed in Example I, having the following ingredients, in weight percent:

		WEIGHT PERCENT
	Graphite (maximum particle size—10 microns)	14
15	Polyvinylpyrrolidone (average molecular weight—10,000)	1.5
	Aqueous Potassium silicate (30° Baume at 68°F —7 centipoises viscosity at 68°) 9.05% K ₂ O and 19.9% SiO ₂	73.1
20	Potassium sodium tartrate	1.4
	Deionized water	10

A glass panel was coated, by spraying, with the above composition and heat cured under identical conditions to those stated in Example I.

Visual inspection of the panel, without magnification, revealed that the surface was a porous mat-appearing layer. The presence of the pores was confirmed by microscopic examination up to 60 diameters magnification, and they appeared to be distributed over the entire surface of the coating. The film was measured and found to have an average thickness of 0.7 mils and an electrical resistance of 122 ohms per square.

Using the same adhesion measurement test described in Example I, the film was found to be substantially harder and more adherent than the coating of Example I. No penetration or flaking of the coating was obtained in the test.

EXAMPLE III

The following compositions employ other film modifiers, in the composition of Example II and each was used in the amount of 1.4 weight percent for comparative purposes. The characteristics of the resulting coatings on glass substrate surfaces are set forth in tabular form below:

	Film Modifier Material	Cured Film Appearance	Cured Film Properties	Cured Film Thickness (Mils)	Cured Film Resistance (ohms per sq.)
50	Potassium Succinate ...	Porous, mat surface	hard, adherent	1.3	56
55	Potassium Oxalate ...	Porous, mat surface	hard, adherent	1.2	65
	Potassium Citrate ...	Porous, mat surface	hard, adherent	1.1	54
	Potassium Acetate ...	Porous, mat surface	hard, adherent	1.3	50
60	Potassium Bitartrate ...	Porous, mat surface	hard, adherent	0.9	38
	Sodium Acetate ...	Porous, mat surface	hard, adherent	1.1	55
65	Sodium Oxalate ...	Porous, mat surface	hard, adherent	1.3	54
	Ammonium Bitartrate	Porous, mat surface	hard, adherent	1.1	44
70	Ammonium Succinate	Porous, mat surface	hard, adherent	1.4	54

The following Examples illustrate additional compositions according to the present invention. These compositions were prepared as described in Example I.

EXAMPLE IV

	WEIGHT PERCENT
5 Graphite—Micronized, natural (average particle size—5 microns)	12
Sodium Silicate Solution, 8.9% Na ₂ O:28.7% SiO ₂ , —1:3.22 S.G. 41° Baume at 68°F	70
Sodium Acetate	2.0
10 Water	14
Polyvinylpyrrolidone (average molecular weight, 40,000)	2.0

EXAMPLE V

	WEIGHT PERCENT
15 Graphite (maximum particle size—200 mesh) ...	16
Potassium Silicate Solution (30° Baume at 68°F, viscosity—7 centipoises at 68°) 9.05% K ₂ O and 19.9% SiO ₂	73
Potassium Bitartrate	5.0
20 Polyvinyl Alcohol (% hydrolysis 87—89, pH 6—8, 5% volatiles)—Viscosity 35—45, cps measured in a 4% water solution at 20°C by the Hocppler falling ball method.	1.5
Water	4.5

EXAMPLE VI

	WEIGHT PERCENT
25 Graphite (maximum particle size—10 microns)	14
Methyl Cellulose	1.5
30 Aqueous Potassium Silicate (30° Baume at 68°F, viscosity—7 centipoises at 68°) 9.05% K ₂ O and 19.9% SiO ₂	73.1
Potassium sodium tartrate	1.4
Deionized water	10

EXAMPLE VII

	WEIGHT PERCENT
35 Graphite (maximum particle size—10 microns)	14
Sodium Carboxymethyl Cellulose	1.5
40 Aqueous Potassium Silicate (30° Baume at 68°F, 7 centipoises viscosity at 68°) 9.05% K ₂ O and 19.9% SiO ₂	73.1
Potassium sodium tartrate	1.4
Deionized water	10

EXAMPLE VIII

	WEIGHT PERCENT
45 Graphite (maximum particle size—10 microns)	14
Hydroxyethyl Cellulose	1.5
50 Aqueous Potassium Silicate (30° Baume at 68°F, —7 centipoises, viscosity at 68°) 9.05% K ₂ O and 19.9% SiO ₂	73.1
Potassium sodium tartrate	1.4
Deionized water	10

WHAT WE CLAIM IS:—

1. A composition for use in forming electrically conductive coatings which comprises, in weight percent, 10% to 25% of a conductive pigment, 15% to 80% of a solution of an alkali metal silicate containing from 42% to 71% water, 0.3% to 5% of

a water-soluble or water-dispersible organic resin material decomposable at the temperatures normally employed in cathode ray tube manufacture, i.e. 250 to 475°C., 0.5% to 10% of an alkali metal or ammonium carboxylic acid salt and the balance water.

2. A composition according to claim 1

which comprises, in weight percent, 12% to 20% of a conductive pigment, 35% to 75% alkali metal silicate containing from 42% to 71% water, 0.75% to 2% of an organic resin as defined in claim 1, 1.0% to 5% of an alkali metal or ammonium carboxylic acid salt and the balance water.

3. A composition according to claim 1 or 2 wherein the alkali metal silicate is potassium silicate.

4. A composition according to any one of claims 1 to 3 wherein the resin is polyvinylpyrrolidone.

5. A composition according to claim 4 wherein the polyvinyl pyrrolidone has a molecular weight of 8,000 to 50,000.

6. A composition according to any one of the preceding claims wherein conductive pigment is graphite having a particle size less than 200 mesh.

7. A composition according to any one of the preceding claims wherein the alkali metal carboxylic acid salt is potassium sodium tartrate.

8. A composition according to claim 1 substantially as hereinbefore described.

9. A composition according to claim 1

substantially as described in any one of Examples 2 to 8.

10. A method for forming an electrically conductive coating on a surface which comprises applying to the surface a composition according to any one of the preceding claims and heat curing the composition on the surface at a temperature within the range of 250° to 475°C. until the coating is hard and adherent to the surface.

11. A method according to claim 10 wherein the said surface is a surface of a cathode ray tube and the amount of the composition used is such that the coating has a thickness in the range of 0.1 to 2 mils.

12. A method according to claim 10 substantially as hereinbefore described.

13. A method according to claim 10 substantially as described in any one of Examples 2 to 8.

14. An article having on a surface thereon of an electrically conductive coating formed thereon by a method as claimed in any one of claims 10 to 13.

J. A. KEMP & CO.,
Chartered Patent Agents,
14, South Square,
Gray's Inn, London, W.C.1.